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International Application No. } PCT/IB02/03759
Demande internationale n° }

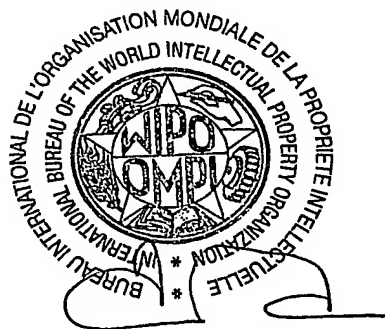
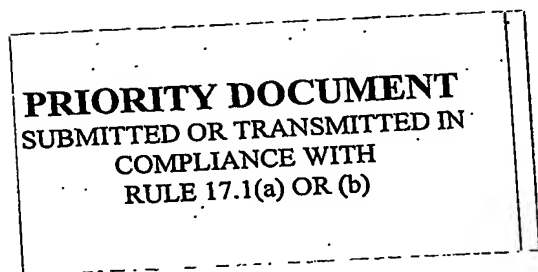
International Filing Date } 11 September 2002
Date du dépôt international } (11.09.02)

Geneva/Genève,

19 September 2003
(19.09.03)

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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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PCT/IB 02 / 03759
International Application No.

11 SEPTEMBER 2002

(11.09.02)

International Filing Date

INTERNATIONAL BUREAU OF WIPO

PCT International Application

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum)

MOL0669-PCT-☒

Box No. I TITLE OF INVENTION		NON-CARBON ANODES FOR ALUMINIUM ELECTRO-WINNING AND OTHER OXIDATION-RESISTANT COMPONENTS WITH IRON OXIDE-CONTAINING COATINGS	
Box No. II APPLICANT		<input type="checkbox"/> This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)		Telephone No.	
MOLTECH Invent S.A. 68-70 Bd de la Pétrusse 2320 LUXEMBOURG		Facsimile No.	
		Teleprinter No.	
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This person is applicant for the purposes of:		<input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
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NGUYEN, Thinh, T. Rte du Grand-Lancy 165b 1213 ONEX SWITZERLAND		<input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)	
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Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)		Telephone No.	
CRONIN, Brian MOLTECH S.A. Rte de Troinex 9 1227 CAROUGE SWITZERLAND		+41 22 343 26 70	
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Sheet No. 2.....

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<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
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State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p> <p>Applicant's registration No. with the Office</p>
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<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p> <p>Applicant's registration No. with the Office</p>
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
<p>This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
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The following designations are hereby made under Rule 4.9(a):

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Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (*Confirmation (including fees) must reach the receiving Office within the 15-month time limit.*)

Box No. VI PRIORITY CLAIM				
The priority of the following earlier application(s) is hereby claimed:				
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1)				
item (2)				
item (3)				
item (4)				
item (5)				
<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.				
The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) <i>(only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office)</i> identified above as:				
<input type="checkbox"/> all items <input type="checkbox"/> item (1) <input type="checkbox"/> item (2) <input type="checkbox"/> item (3) <input type="checkbox"/> item (4) <input type="checkbox"/> item (5) <input type="checkbox"/> other, see Supplemental Box				
<i>* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):</i>				
Box No. VII INTERNATIONAL SEARCHING AUTHORITY				
Choice of International Searching Authority (ISA) <i>(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):</i>				
ISA / EP				
Request to use results of earlier search; reference to that search <i>(if an earlier search has been carried out by or requested from the International Searching Authority):</i>				
Date (day/month/year)		Number	Country (or regional Office)	
Box No. VIII DECLARATIONS				
The following declarations are contained in Boxes Nos. VIII (i) to (v) <i>(mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):</i>				Number of declarations
<input type="checkbox"/> Box No. VIII (i)	Declaration as to the identity of the inventor			:
<input type="checkbox"/> Box No. VIII (ii)	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent			:
<input type="checkbox"/> Box No. VIII (iii)	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application			:
<input type="checkbox"/> Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)			:
<input type="checkbox"/> Box No. VIII (v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty			:

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:

(a) the following number of sheets in paper form:

request (including declaration sheets) : 5
 description (excluding sequence listing part) : 15
 claims : 6
 abstract : 1
 drawings : _____

Sub-total number of sheets : 27

sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below) : _____

Total number of sheets : 27

(b) sequence listing part of description filed in computer readable form

- (i) ☐ only (under Section 801(a)(i))
 (ii) ☐ in addition to being filed in paper form (under Section 801(a)(ii))

Type and number of carriers (diskette, CD-ROM, CD-R or other) on which the sequence listing part is contained (additional copies to be indicated under item 9(ii), in right column):

This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):

1. ☐ fee calculation sheet :
 2. ☐ original separate power of attorney :
 3. ☐ original general power of attorney :
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 5. ☐ statement explaining lack of signature :
 6. ☐ priority document(s) identified in Box No. VI as item(s): :
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Number of items

Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

English

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).



CRONIN, Brian - Agent

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1. Date of actual receipt of the purported international application:

11 SEPTEMBER 2002

(11.09.02)

3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:

4. Date of timely receipt of the required corrections under PCT Article 11(2):

5. International Searching Authority (if two or more are competent):

ISA / EP

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NON-CARBON ANODES FOR ALUMINIUM ELECTROWINNING
AND OTHER OXIDATION RESISTANT COMPONENTS
WITH IRON OXIDE-CONTAINING COATINGS

Field of the Invention

This invention relates to a method of manufacturing non-carbon anodes for use in aluminium electrowinning cells as well as other oxidation resistant components.

5

Background Art

Using non-carbon anodes - i.e. anodes which are not made of carbon as such, e.g. graphite, coke, etc., but possibly contain carbon in a compound - for the electrowinning of aluminium should drastically improve the aluminium production process by reducing pollution and the cost of aluminium production. Many attempts have been made to use oxide anodes, cermet anodes and metal-based anodes for aluminium production, however they were never adopted by the aluminium industry.

15

For the dissolution of the raw material, usually alumina, a highly aggressive fluoride-based electrolyte, such as cryolite, is required.

Materials for protecting aluminium electrowinning components have been disclosed in US Patents 5,310,476, 5,340,448, 5,364,513, 5,527,442, 5,651,874, 6,001,236, 6,287,447 and in PCT publication WO01/42531 (all assigned to MOLTECH). Such materials are predominantly made (more than 50%) of non-oxide ceramic materials, e.g. borides, carbides or nitrides, and are suitable for exposure to molten aluminium and to a molten fluoride-based electrolyte. However, these non-oxide ceramic-based materials do not resist exposure to anodically produced nascent oxygen.

The materials having the greatest resistance to oxidation are metal oxides which are all to some extent soluble in cryolite. Oxides are also poorly electrically conductive, therefore, to avoid substantial ohmic losses

and high cell voltages, the use of oxides should be minimal in the manufacture of anodes. Whenever possible, a good conductive material should be utilised for the anode core, whereas the surface of the anode is preferably made of an oxide having a high electrocatalytic activity.

Several patents disclose the use of an electrically conductive metal anode core with an oxide-based active outer part, in particular US patents 4,956,069, 4,960,494, 5,069,771 (all Nguyen/Lazouni/Doan), 6,077,415 (Duruz/de Nora), 6,103,090 (de Nora), 6,113,758 (de Nora/Duruz) and 6,248,227 (de Nora/Duruz), as well as PCT publications WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804 (Crottaz/Duruz), WO00/40783 (de Nora/Duruz), WO01/42534 (de Nora/Duruz) and WO01/42536 (Nguyen/Duruz/de Nora).

US patents 4,039,401 and 4,173,518 (both Yamada/Hashimoto/Horinouchi) disclose multiple oxides for use as electrochemically active anode material for aluminium electrowinning. The multiple oxides include inter-alia oxides of iron, nickel, titanium and yttrium, such as NiFe_2O_4 or TiFe_2O_4 , in US 4,039,401, and oxides of yttrium, iron, titanium and tantalum, such as $\text{Fe}_2\text{O}_3 \cdot \text{Ta}_2\text{O}_5$, in US 4,173,518. The multiple oxides are produced by sintering their constitutive single oxides and then they are crushed and applied onto a metal substrate (titanium, nickel or copper) by spraying or dipping. Alternatively, the multiple oxides can be produced by electroplating onto the metal substrate the constitutive metals of the multiple oxides followed by an oxidation treatment.

Likewise US patents 4,374,050 and 4,374,761 (both Ray) disclose non-stoichiometric multiple oxides for use as electrochemically active anode material for aluminium electrowinning. The multiple oxides include inter-alia oxides of nickel, titanium, tantalum, yttrium and iron, in particular nickel-iron oxides. The multiple oxides are produced by sintering their constitutive single oxides and then they can be cladded onto a metal substrate.

WO99/36591 (de Nora), WO99/36593 and WO99/36594 (both Duruz/de Nora) disclose sintered multiple oxide

coatings applied onto a metal substrate from a slurry containing particulate of the multiple oxides in a colloidal and/or inorganic polymeric binder, in particular colloidal or polymeric alumina, ceria, lithia, 5 magnesia, silica, thoria, yttria, zirconia, tin oxide or zinc oxide. The multiple oxides include ferrites of cobalt, copper, chromium, manganese, nickel and zinc. It is mentioned that the coating can be obtained by reacting precursors thereof among themselves or with constituents 10 of the substrate.

US patent 6,372,119 and WO01/31091 (both Ray/Liu/Weirauch) disclose a cermet made from sintered particles of nickel, iron and cobalt oxides and of metallic copper and silver possibly alloyed with cobalt, nickel, iron, 15 aluminium, tin, niobium, tantalum, chromium molybdenum or tungsten. The particles can be applied as a coating onto an anode substrate and sintered thereon to form an anode for the electrowinning of aluminium.

20 These non-carbon anodes have not as yet been commercially and industrially applied and there is still a need for metal-based anodes for aluminium production.

Summary of the Invention

The present invention relates primarily to a method of forming a hematite-containing protective layer on a 25 metal-based substrate for use in a high temperature oxidising and/or corrosive environment. The method comprises: (I) applying onto the substrate a particle mixture consisting of: (a) 60 to 95 weight%, in particular 70 to 85 weight%, of hematite particles; (b) 5 30 to 25 weight%, in particular 8 to 20 weight%, of nitride and/or carbide particles, such as boron nitride, aluminium nitride, silicon nitride, silicon carbide, tungsten carbide or zirconium carbide particles; and (c) 0 to 15 weight%, in particular 5 to 15 weight%, of 35 particles of one or more further constituents that consist of at least one metal or metal oxide or a heat-convertible precursor thereof; and (II) sintering the hematite particles by heat treating the particle mixture to form the protective layer that is made of a 40 microporous sintered hematite matrix in which the nitride

and/or carbide particles are embedded and which contains, when present, said one or more further constituents.

When hematite particles are sintered among themselves by heat treatment, they undergo a volume contraction which results in the formation of cracks.

However, it has been observed that the addition of minor amounts of carbide and/or nitride particles to the hematite particles inhibits the formation of such cracks during sintering.

Without being bound to any theory, it is believed that these carbide/nitride particles are chemically substantially inert during the sintering process. However, their presence physically inhibits aggregation of the voids formed by the sintering contraction of the hematite-based material. Thus, instead of forming compact portions of hematite separated by cracks formed by aggregation of voids, the sintering process with the carbide/nitride particles produces a continuous crack-free hematite-based material having throughout a homogeneous microporosity. This microporosity results from the local sintering contraction of the hematite which forms micropores that are inhibited from significantly migrating in the hematite-based material by the presence of the carbide/nitride particles that act as barriers against significant pore migration.

Nitrides and carbides being less resistant to oxidation than hematite, the amount of nitride/carbide particles in the particle mixture is preferably maintained at a low value, e.g. below 20 or even below 15 weight%. However, when the protective layer is exposed to oxidation conditions that are less severe than when it is used as an active anode coating for aluminium production, the protective layer can contain up to 25 weight% nitride/carbide particles.

The electrical/electrochemical properties of the protective layer can be improved by selecting at least one of the further constituents from oxides of titanium, yttrium, ytterbium, tantalum, manganese, zinc, zirconium, cerium and nickel and/or a heat-convertible precursor

thereof. Such selected further constituents can be present in the protective layer in a total amount of 1 to 15 weight%. Usually, it is sufficient for these selected further constituents to be present in a catalytic amount to achieve the electrical/electrochemical effect, in particular in a total amount of 5 to 12 weight%.

The protective layer can alternatively or additionally comprise at least one of the further constituents selected from metallic Cu, Ag, Pd, Pt, Co, Cr, Al, Ga, Ge, Hf, In, Ir, Mo, Mn, Nb, Re, Rh, Ru, Se, Si, Sn, Ti, V, W, Li, Ca, Ce and Nb and/or an oxide thereof which can be added to the particle mixture as such or as a precursor, in the form of particles or in solution, for example a salt such as a chloride, sulfate, nitrate, chlorate or perchlorate, or a metal organic compound such as an alkoxide, formate or acetate. These selected further constituents can be present in the protective layer in a total amount of 0.5 to 15 weight%, preferably from 0.5 to 5 weight%, in particular from 1 to 3 weight%.

Minor amounts of copper or copper oxides, i.e. up to 3 or 5 weight%, improve the electrical conductivity of the protective layer and diffusion of iron oxide (and possibly other oxides) during the sintering of the protective layer. This leads to the production of more conductive and denser protective layers than without the use of copper metal and/or oxides.

Limiting the amount of further constituents also reduces the risk of contamination of the protective layer's environment during use, e.g. an electrolyte of a metal electrowinning cell.

The particle mixture can be made of particles that are smaller than 75 micron, preferably smaller than 50 micron, in particular from 5 to 45 micron.

The substrate can be metallic, ceramic, a cermet of a surface-oxidised metal.

Usually, the substrate comprises at least one metal selected from chromium, cobalt, hafnium, iron,

molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and zirconium or an oxide thereof. For instance, the substrate comprises an alloy of iron, in particular an iron-nickel alloy optionally containing at least one further element selected from cobalt, copper, aluminium, yttrium, manganese, silicon and carbon.

Advantageously, the method of the invention comprises oxidising the surface of a metallic substrate to form an integral anchorage layer thereon to which the protective layer is bonded by sintering during heat treatment, in particular an integral layer containing an oxide of iron and/or another metal, such as nickel, that is sintered during the heat treatment with iron oxide from the particle mixture. Further details on such an anchoring of the protective layer are disclosed in PCT/IB02/01239 (Nguyen/de Nora).

When used for aluminium electrowinning, the protected metal-based substrate preferably contains at least one metal selected from nickel, iron, cobalt, copper, aluminium and yttrium. Suitable alloys for such a metal-based substrate are disclosed in US Patent 6,372,099 (Duruz/de Nora), and WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804 (Crottaz/Duruz), WO01/42534 (de Nora/Duruz), WO01/42536 (Duruz/Nguyen/de Nora), PCT/IB01/01241 (Nguyen/de Nora), PCT/IB01/01838 (Nguyen/Duruz/de Nora) and PCT/IB02/00820 (Nguyen/de Nora).

The particle mixture can be applied onto the substrate in a slurry. Such a slurry may comprise an organic binder which is at least partly volatilised during sintering, in particular a binder selected from polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, hexanol, butyl benzyl phthalate and ammonium polymethacrylate. The slurry may also comprise an inorganic binder, in particular a colloid, such as a colloid selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia,

indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of colloids; and/or an
5 inorganic polymer, such as a polymer selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thoria, and
10 precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of inorganic polymers. Such an inorganic binder may be sintered during the heat treatment with an oxide of an anchorage layer which is integral with the metal-based substrate to bind
15 the protective layer to the metal-based substrate.

Typically, the particle mixture is consolidated on the substrate by heat treatment at a temperature in the range from 800° to 1400°C, in particular from 850° to 1150°C. The particle mixture can be consolidated on the
20 substrate by heat treatment for 1 to 48 hours, in particular for 5 to 24 hours. Usually, the particle mixture is consolidated on the substrate by heat treatment in an atmosphere containing 10 to 100 mol% O₂.

Further details on the application of inorganic
25 colloidal and/or polymeric slurries on metal substrates are disclosed in US Patents 6,361,681 (de Nora/Duruz) and 6,365,018 (de Nora) and in PCT/IB02/01239 (Nguyen/de Nora).

Typically, the component of the invention is a
30 component of a cell for the electrowinning of a metal such as aluminium, in particular a current carrying anodic component such as an active anode structure or an anode stem, or another cell component exposed to molten electrolyte and/or cell fumes, such as a cell cover or a
35 powder feeder. Examples of such cell components are disclosed in W000/40781 and W000/40782 (both de Nora), W000/63464 (de Nora/Berclaz), W001/31088 (de Nora) and PCT/IB02/00669 (de Nora/Berclaz). The applied layers on such cell components can be consolidated before use by
40 heat treating the components over a cell.

Advantageously, the particle mixture can be consolidated by heat treating the cell component over the cell to form the protective layer. By carrying out the consolidation heat-treatment immediately before use, thermal shocks and stress caused by cooling and re-heating of the component between consolidation and use can be avoided.

Another aspect of the invention relates to a method of electrowinning a metal such as aluminium. The method comprises manufacturing by the above described method a current-carrying anodic component protected by a protective layer, installing the anodic component in a molten electrolyte containing a dissolved salt of the metal to electrowin, such as alumina, and passing an electrolysis current from the anodic component to a facing cathode in the molten electrolyte to evolve oxygen anodically and produce the metal cathodically.

The electrolyte can be a fluoride-based molten electrolyte, in particular containing fluorides of aluminium and sodium. Further details of suitable electrolyte compositions are for example disclosed in PCT/IB02/01952 (Nguyen/de Nora).

The cell can be operated with an electrolyte maintained at a temperature in the range from 800° to 960°C, in particular from 880° to 940°C.

Preferably, to reduce the solubility of metal-based cell components, an alumina concentration which is at or close to saturation is maintained in the electrolyte, particularly adjacent the anodic component.

An amount of iron species can also be maintained in the electrolyte to inhibit dissolution of the protective layer of the anodic component. Further details on such a cell operation are disclosed in the above mentioned US Patent 6,372,099.

The invention relates also to method of electrowinning a metal such as aluminium. The method comprises manufacturing by the above disclosed method a cover protected by a protective layer, placing the cover

over a metal production cell trough containing a molten electrolyte in which a salt of the metal to electrowin is dissolved, passing an electrolysis current in the molten electrolyte to evolve oxygen anodically and metal cathodically, and confining electrolyte vapours and evolved oxygen within the cell trough by means of the protective layer of the cover.

Further features of cell covers are disclosed in US Patent 6,402,928 (de Nora/Sekhar), PCT/IB02/00669 (de Nora/Berclaz) and PCT/IB02/02018.

A further aspect of the invention relates to a hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment. The protective layer on the substrate is producible by the above described method.

Yet a further aspect of the invention concerns a cell for the electrowinning of a metal, such as aluminium, having at least one component that comprises a metal-based substrate covered with a hematite-containing protective layer as defined above.

In a modification of the invention, the above hematite-containing mixture can be shaped into a body and sintered as discussed below.

Detailed Description

Examples of starting compositions of particle mixtures for producing protective layers according to the invention are given in Table 1, which shows the weight percentages of the indicated constituents for each specimen A1-L1. Examples of alloy compositions of substrates for application of protective layers according to the invention are given in Table 2, which shows the weight percentages of the indicated metals for each specimen A2-O2.

TABLE 1

	Fe ₂ O ₃	BN	AlN	ZrC	TiO ₂	ZrO ₂	ZnO	Ta ₂ O ₅	CuO
A1	78	10	--	--	10	--	--	--	2
B1	78	10	--	--	--	--	10	--	2
C1	70	18	--	--	--	--	10	--	2
D1	78	10	--	--	--	10	--	--	2
E1	80	10	--	--	--	--	--	--	10
F1	78	10	--	--	--	--	--	10	2
G1	78	--	10	--	10	--	--	--	2
H1	78	--	12	--	--	--	5	3	2
I1	70	10	4	3	--	2	5.5	3	2.5
J1	75	14	--	--	5	5	--	--	1
K1	85	5	4	--	--	--	6	--	--
L1	75	--	--	12	5	--	--	5	3

TABLE 2

	Ni	Fe	Co	Cu	Al	Y	Mn	Si	C
A2	48	38	--	10	3	--	0.5	0.45	0.05
B2	49	40	--	7	3	--	0.5	0.45	0.05
C2	36	50	--	10	3	--	0.5	0.45	0.05
D2	36	50	--	10	3	0.35	0.3	0.3	0.05
E2	36	53	--	7	3	--	0.5	0.45	0.05
F2	36	53	--	7	3	0.35	0.3	0.3	0.05
G2	48	38	--	10	3	0.35	0.3	0.3	0.05
H2	22	68	--	5.5	4	--	0.25	0.2	0.05
I2	42	42	--	12	2	1	0.5	0.45	0.05
J2	42	40	--	12.5	4	0.4	0.45	0.6	0.05
K2	45	44	--	7	3	--	0.5	0.45	0.05
L2	30	69	--	--	--	--	0.5	0.45	0.05
M2	25	65	7	1	1	--	0.5	0.45	0.05
N2	55	32	--	10	2	0.2	0.3	0.45	0.05
O2	55	32	--	10	2	--	0.45	0.5	0.05

Comparative Example 1

5 An anode was manufactured from an anode rod of diameter 20 mm and total length 20 mm made of a cast alloy having the composition of sample A2 of Table 2. The anode rod was supported by a stem made of an alloy containing nickel, chromium and iron, such as Inconel, 10 protected with an alumina sleeve. The anode was suspended for 16 hours over a molten cryolite-based electrolyte at 925°C whereby its surface was oxidised.

Electrolysis was carried out by fully immersing the anode rod in the molten electrolyte. The electrolyte

contained 18 weight% aluminium fluoride (AlF_3), 6.5 weight% alumina (Al_2O_3) and 4 weight% calcium fluoride (CaF_2), the balance being cryolite (Na_3AlF_6).

5 The current density was about 0.8 A/cm² and the cell voltage was at 3.5-3.8 volt throughout the test. The concentration of dissolved alumina in the electrolyte was maintained during the entire electrolysis by periodically feeding fresh alumina into the cell.

10 After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

The anode's outer dimensions had remained substantially unchanged. The anode's oxide outer part had grown from an initial thickness of about 70 micron to a
15 thickness after use of about up to 500 micron.

Samples of the used electrolyte and the product aluminium were also analysed. It was found that the electrolyte contained 150-280 ppm nickel and the product aluminium contained roughly 1000 ppm nickel.

20 Comparative Example 2

Another comparative aluminium electrowinning anode was prepared according to the invention as follows:

A slurry for coating an anode substrate was prepared by suspending in 32.5 g of an aqueous solution containing
25 5 weight% polyvinyl alcohol (PVA) 67.5 g of a nitride/carbide-free particle mixture made of 86 weight% Fe_2O_3 particles, 10 weight% TiO_2 particles and 2 weight% CuO particles (with particle sizes of -325 mesh, i.e. smaller than 44 micron).

30 An anode substrate made of the alloy of sample A2 of Table 2 was covered with six layers of this slurry that were applied with a brush. The applied layers were dried for 10 hours at 140°C in air and then consolidated at 950°C for 16 hours to form a hematite-based coating which
35 had a thickness of 0.24 to 0.26 mm.

During consolidation, the Fe_2O_3 particles were sintered together into a matrix with a volume contraction. Pores formed by this contraction had agglomerated to form small cracks that had a length of the order of 1.5 mm and a width of up to 20 micron. The TiO_2 particles and CuO particles were dissolved in the sintered Fe_2O_3 .

Example 1

An aluminium electrowinning anode was prepared according to the invention as follows:

A slurry for coating an anode substrate was prepared by suspending in 32.5 g of an aqueous solution containing 5 weight% polyvinyl alcohol (PVA) 67.5 g of a particle mixture made of hematite Fe_2O_3 particles, boron nitride particles, TiO_2 particles and CuO particles (with particle size of -325 mesh, i.e. smaller than 44 micron) in a weight ratio corresponding to sample A1 of Table 1.

An anode substrate made of the alloy of sample A2 of Table 2 was covered with ten layers of this slurry that were applied with a brush. The applied layers were dried for 10 hours at 140°C in air and then consolidated at 950°C for 16 hours to form a protective hematite-based coating which had a thickness of 0.4 to 0.45 mm.

During consolidation, the Fe_2O_3 particles were sintered together into a microporous matrix with a volume contraction. The TiO_2 particles and CuO particles were dissolved in the sintered Fe_2O_3 . The boron nitride particles remained substantially inert during the sintering but prevented migration and agglomeration of the micropores into cracks. Hence, as opposed to Comparative Example 2, the hematite-containing protective layer was crack-free even though it was thicker, and thus this boron nitride-containing hematite layer was able better to inhibit diffusion from and to the metal-based substrate.

Underneath the coating, an integral oxide scale mainly of iron oxide had grown from the substrate during the heat treatment and sintered with iron oxide and

titanium oxide from the coating to firmly anchor the coating to the substrate. The sintered integral oxide scale contained titanium oxide in an amount of about 10 metal weight%. Minor amounts of copper, aluminium and
5 nickel were also found in the oxide scale (less than 5 metal weight% in total).

Example 2

An anode was prepared as in Example 1 by covering an iron-alloy substrate with layers of a slurry containing a
10 particle mixture of Fe_2O_3 , BN, TiO_2 and CuO.

The applied layers were dried and then consolidated by suspending the anode for 16 hours over a cryolite-based electrolyte at about 925°C . The electrolyte contained 18 weight% aluminium fluoride (AlF_3), 6.5
15 weight% alumina (Al_2O_3) and 4 weight% calcium fluoride (CaF_2), the balance being cryolite (Na_3AlF_6).

Upon consolidation of the layers, the anode was immersed in the molten electrolyte and an electrolysis current was passed from the anode to a facing cathode
20 through the alumina-containing electrolyte to evolve oxygen anodically and produce aluminium cathodically. A high oxygen evolution was observed during the test. The current density was about 0.8 A/cm^2 and the cell voltage was stable at 3.1-3.2 volt throughout the test.

Compared to an uncoated anode, i.e. the anode of comparative Example 1, the coating of an alloy-anode with an oxide protective layer according to the invention led to an improvement of the anode performance such that the
25 cell voltage was stabilised and also reduced by 0.4 to 0.6 volt, which corresponds to about 10 to 20%, thus
30 permitting tremendous energy savings.

After 50 hours, the anode was extracted from the electrolyte and underwent cross-sectional examination.

The dimension of the coating had remained
35 substantially unchanged. However, TiO_2 had selectively been dissolved in the electrolyte from the protective coating. The integral oxide layer of the anode substrate

had grown to a thickness of 200 micron, i.e. at a much slower rate than the oxide layer of the uncoated anode of Comparative Example 1.

5 Samples of the used electrolyte and the product aluminium were also analysed. It was found that the electrolyte contained less than 70 ppm nickel and the produced aluminium contained less than 300 ppm nickel which is significantly lower than with the uncoated anode of Comparative Example 1. This demonstrated that the
10 protective coating of the invention constituted an efficient barrier reducing nickel dissolution from the anode's alloy, inhibiting contamination of the product aluminium by nickel.

Example 3

15 Examples 1 and 2 can be repeated using different combinations of coating compositions (A1-L1) selected from Table 1 and metal alloy compositions (A2-O2) selected from Table 2.

20 While the invention has been described in conjunction with specific embodiments thereof, it is evident that alternatives, modifications, and variations will be apparent to those skilled in the art.

For example, in a modification of the invention, all the materials described above for forming the hematite-containing protective layers can alternatively be shaped
25 into a body and sintered to form a massive component, in particular an aluminium electrowinning anode, made of the hematite-containing material. Such a component can be made of oxides or, especially when used as a current
30 carrying component, of a cermet having a metal phase for improving the electrical conductivity of the material.

CLAIMS

1. A method of forming a hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment:
5 comprising:
- applying onto the substrate a particle mixture consisting of:
(a) 60 to 95 weight%, in particular 70 to 85 weight%, of hematite particles;
10 (b) 5 to 25 weight%, in particular 8 to 20 weight%, of nitride and/or carbide particles; and
(c) 0 to 15 weight%, in particular 5 to 15 weight%, of particles of one or more further constituents that consist of at least one metal or metal oxide or a
15 heat-convertible precursor thereof;
and
- sintering the hematite particles by heat treating the particle mixture to form the protective layer that is made of a microporous sintered hematite matrix in which
20 the nitride and/or carbide particles are embedded and which contains, when present, said one or more further constituents.
2. The method of claim 1, wherein said nitride and/or carbide particles are selected from boron nitride,
25 aluminium nitride, silicon nitride, silicon carbide, tungsten carbide and zirconium carbide, and mixtures thereof.
3. The method of claim 1 or 2, wherein said one or more further constituents are selected from oxides of
30 titanium, yttrium, ytterbium, tantalum, manganese, zinc, zirconium, cerium and nickel and/or heat-convertible precursors thereof.
4. The method of claim 3, wherein the selected further constituent(s) of claim 3 is/are present in the
35 protective layer in a total amount of 1 to 15 weight%, preferably 5 to 12 weight%.
5. The method of any preceding claim, wherein said one or more further constituents are selected from metallic

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Cu, Ag, Pd, Pt, Co, Cr, Al, Ga, Ge, Hf, In, Ir, Mo, Mn, Nb, Re, Rh, Ru, Se, Si, Sn, Ti, V, W, Li, Ca, Ce and Nb and oxides thereof, and/or heat-convertible precursors thereof.

- 5 6. The method of claim 5, wherein the selected further constituent(s) of claim 5, in particular copper and/or copper oxide, is/are present in a total amount of 0.5 to 15 weight%, preferably from 0.5 to 5 weight, in particular from 1 to 3 weight%.
- 10 7. The method of any preceding claim, wherein the particle mixture is made of particles that are smaller than 75 micron, preferably smaller than 50 micron, in particular from 5 to 45 micron.
- 15 8. The method of any preceding claim, wherein the substrate is metallic, a ceramic, a cermet or metallic with an integral oxide layer.
- 20 9. The method of any preceding claim, wherein the substrate comprises at least one metal selected from chromium, cobalt, hafnium, iron, molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and zirconium.
- 25 10. The method of claim 9, wherein the substrate comprises an alloy of iron, in particular an iron-nickel alloy optionally containing at least one further element selected from cobalt, copper, aluminium, yttrium, manganese, silicon and carbon.
- 30 11. The method of any preceding claim, comprising oxidising the surface of a metallic substrate to form an integral anchorage layer thereon to which the protective layer is bonded by sintering during heat treatment, in particular an integral layer containing an oxide of iron and/or another metal, such as nickel, that is sintered during heat treatment with iron oxide from the particle mixture.
- 35 12. The method of any preceding claim, wherein the particle mixture is applied in a slurry onto the substrate.

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13. The method of claim 12, wherein the slurry comprises an organic binder, in particular a binder selected from polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, hexanol, butyl benzyl phthalate and ammonium polymethacrylate.

14. The method of claim 12 or 13, wherein the slurry comprises an inorganic binder, in particular a colloid, such as a colloid selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of colloids; and/or an inorganic polymer, such as a polymer selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of inorganic polymers.

15. The method of claim 14, wherein the inorganic binder is sintered during the heat treatment with an oxide of an anchorage layer which is integral with the substrate to bind the protective layer to the substrate.

16. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat treatment at a temperature in the range from 800° to 1400°C, in particular from 850° to 1150°C.

17. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat treatment for 1 to 48 hours, in particular for 5 to 24 hours.

18. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat treatment in an atmosphere containing 10 to 100 mol% O₂.
- 5 19. The method of any preceding claim for manufacturing a component of a metal electrowinning cell, in particular an aluminium electrowinning cell, which during use is exposed to molten electrolyte and/or cell fumes and protected therefrom by said protective layer.
- 10 20. The method of claim 19 for manufacturing a current carrying anodic component, in particular an active anode structure or an anode stem.
21. The method of claim 19 for manufacturing a cover.
- 15 22. The method of any one of claims 19 to 21, comprising consolidating the particle mixture to form the protective layer by heat treating the cell component over the cell.
- 20 23. A method of electrowinning a metal, such as aluminium, comprising manufacturing a current-carrying anodic component protected by said protective layer as defined in claim 19, installing the anodic component in a molten electrolyte containing a dissolved salt of the metal to electrowin such as alumina, and passing an electrolysis current from the anodic component to a facing cathode in the molten electrolyte to evolve oxygen anodically and produce the metal cathodically.
- 25 24. The method of claim 23, wherein the electrolyte is a fluoride-based molten electrolyte, in particular containing fluorides of aluminium and sodium.
- 30 25. The method of claim 23 or 24, comprising maintaining the electrolyte at a temperature in the range from 800° to 960°C, in particular from 880° to 940°C.
26. The method of any one of claims 23 to 25, comprising maintaining in the electrolyte, particularly adjacent the anodic component, an alumina concentration which is at or close to saturation.

27. The method of any one of claims 23 to 26, comprising maintaining an amount of iron species in the electrolyte to inhibit dissolution of the protective layer of the anodic component.

5 28. A method of electrowinning a metal, such as aluminium, comprising manufacturing a cover protected by said protective layer as defined in claim 21, placing the cover over a metal electrowinning cell trough containing a molten electrolyte in which a salt of the metal to
10 electrowin is dissolved, passing an electrolysis current in the molten electrolyte to evolve oxygen anodically and the metal cathodically, and confining electrolyte vapours and evolved oxygen within the cell trough by means of the protective layer of the cover.

15 29. A hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment, producible by the method of any one of claims 1 to 22, which is microporous and at least substantially crack-free and contains nitride
20 and/or carbide particles.

30. A cell for the electrowinning of a metal, such as aluminium, having at least one component that comprises a metal-based substrate covered with a hematite-containing protective layer as defined in claim 29.

25 31. A method of forming a hematite-containing body for use in a high temperature oxidising and/or corrosive environment: comprising:

- providing a particle mixture consisting of:

- 30 (a) 60 to 95 weight%, in particular 70 to 85 weight%, of hematite particles;
- (b) 5 to 25 weight%, in particular 8 to 20 weight%, of nitride and/or carbide particles; and
- 35 (c) 0 to 15 weight%, in particular 5 to 15 weight%, of particles of one or more further constituents that consist of at least one metal or metal oxide or a heat-convertible precursor thereof;

- shaping the particle mixture into the body;
and

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5 - sintering the hematite particles by heat treating the particle mixture to form the hematite-containing body that is made of a microporous sintered hematite matrix in which the nitride and/or carbide particles are embedded and which contains, when present, said one or more further constituents.

10 32. The method of claim 31, incorporating any of the features of claims 2 to 7 and/or wherein the particle mixture is provided in a slurry and consolidated as defined in any one of claims 13, 14, 16, 17 or 18.

33. The method of claim 31 or 32, for manufacturing a component as defined in claims 19 to 21.

BEST AVAILABLE COPY**ABSTRACT**

A method of forming a dense and crack-free hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment comprises applying onto the substrate a particle mixture consisting of: 60 to 95 weight%, in particular 70 to 85 weight%, of hematite particles; 5 to 25 weight%, in particular 8 to 20 weight%, of nitride and/or carbide particles, such as boron nitride, aluminium nitride or zirconium carbide particles; and 0 to 15 weight%, in particular 5 to 15 weight%, of particles of one or more further constituents that consist of at least one metal or metal oxide or a heat-convertible precursor thereof. The hematite particles are then sintered by heat treating the particle mixture to form the protective layer that is made of a microporous sintered hematite matrix in which the nitride and/or carbide particles are embedded and which contains, when present, said one or more further constituents. The mechanical, electrical and electrochemical properties of the protective layer can be improved by using an oxide of titanium, zinc, zirconium or copper. Typically, the protected substrate can be used in a cell for the electrowinning of a metal such as aluminium.